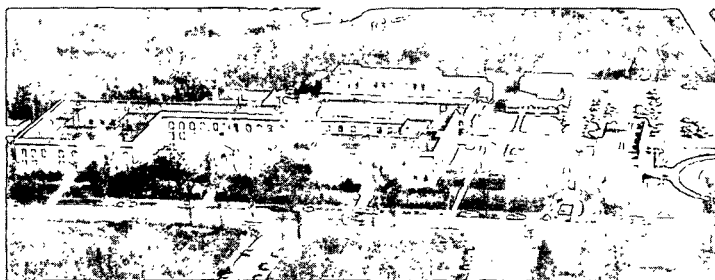


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AN ANOMERIC EFFECT IN PHOTOCHEMICAL HYDROGEN
ABSTRACTION REACTIONS OF TETRAHYDROPYRANYL ETHERS

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AN ANOMERIC EFFECT IN PHOTOCHEMICAL HYDROGEN ABSTRACTION
REACTIONS OF TETRAHYDROPYRANYL ETHERS

Ronald D. McKelvey and Kim Hayday

INTRODUCTION MacMillan Bledel Research Limited
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The degradation of cellulose by ultraviolet light caused yellowing and a loss in strength and stability of paper. This is most evident in the yellowing of groundwood when exposed to sunlight. Earlier model compound studies in this series showed that two reactions at the anomeric carbon are probably important in cellulose degradation. The present model compound system allowed an evaluation of the effect of configuration at the anomeric carbon on photochemical reactivity.

This paper is being submitted to the Journal of the American Chemical Society for publication.

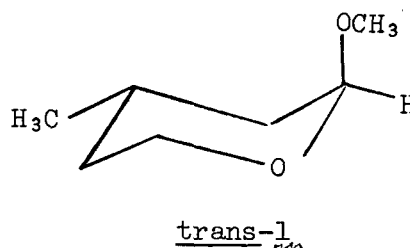
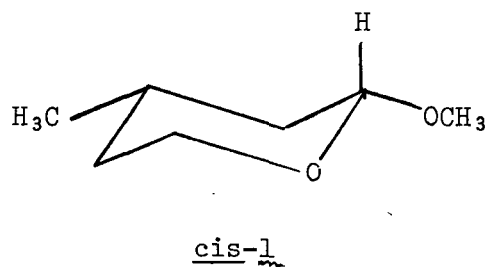
ABSTRACT

Hydrogen-atom abstraction from 2-methoxy-4-methyltetrahydropyran (1) by photochemically excited benzophenone in benzene gave methyl 3-methyl-5-phenylvalerate and 3-methyl- δ -valerolactone. The cis-isomer of 1 was 8.0 times as reactive as the trans-isomer, indicating that abstraction of an axial hydrogen atom is more favorable than abstraction of an equatorial hydrogen. This observation is rationalized in terms of antiperiplanar overlap of the carbon-hydrogen bond being broken with nonbonding orbitals on both oxygens. The two isomers of 1 did not interconvert during irradiation, indicating that the initial hydrogen abstraction is irreversible.

An Anomeric Effect in Photochemical Hydrogen Abstraction Reactions
of Tetrahydropyranyl Ethers¹

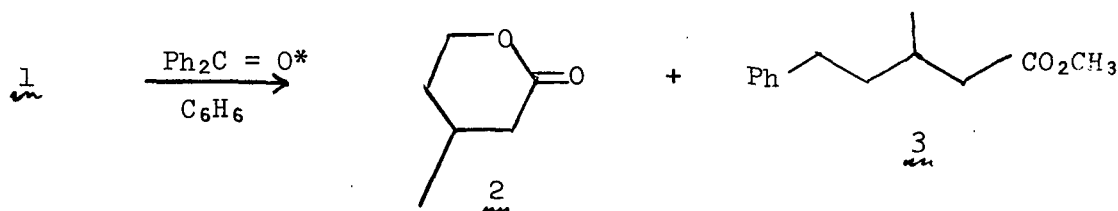
Sir:

In our previous paper² on excited-state ketone initiated hydrogen abstraction reactions of 2-methoxytetrahydropyran, there was some indication that conformational effects might be important. Cis- and trans-2-methoxy-4-methyltetrahydropyran (1) exist primarily in single conformations,³ and therefore provide an ideal system for studying these effects. The cis-isomer exists almost completely in the conformation having the methoxy group equatorial since, in the alternative conformation, a severe 1,3-diaxial interaction between the methyl and methoxy groups is unfavorable. On the other hand, the trans-isomer exists almost completely in the conformation with the methyl group in the more favorable equatorial position and the methoxy group axial, which is favored due to the anomeric effect.



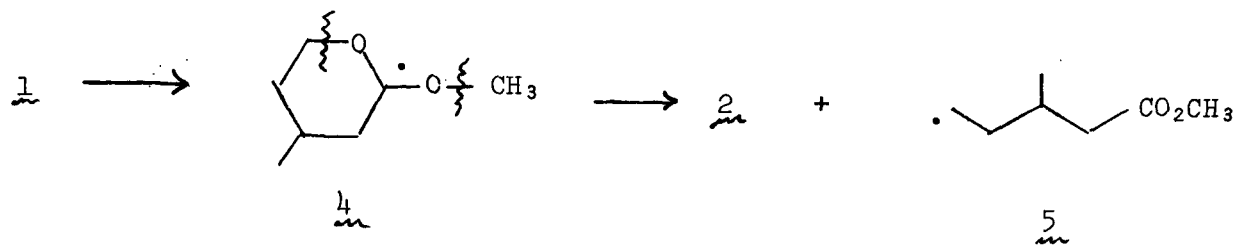
A mixture of cis- and trans-1 was prepared according to literature procedures⁴ and a portion was separated by gas chromatography.⁵ Assignment of the isomers, based on nmr of the "anomeric" hydrogen, was in agreement with the literature.⁴

Irradiation⁶ of mixtures of benzophenone and either the individual isomers of 1, or an isomeric mixture in benzene gave 3-methyl- δ -valerolactone (2) and methyl 3-methyl-5-phenylvalerate (3).⁷



The ratio of these products varied somewhat with conditions and will be reported on fully in our full paper but, in general, less than 50% of the consumed 1 could be accounted for by these two products. Interestingly, no methyl 3-methylvalerate was detected⁸ for irradiations in benzene, even though the corresponding product was found previously in the 2-methoxytetrahydropyran system.²

The products are analogous to those observed previously² in the 2-methoxytetrahydropyran system, and can be rationalized by initial hydrogen abstraction by excited benzophenone to give free radical 4, which can then undergo carbon-oxygen bond cleavage in either of two modes to give lactone 2 or open-chain radical 5 which reacts with solvent to give 3.



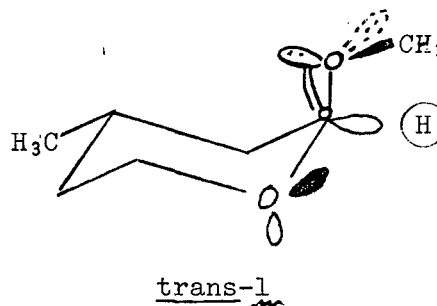
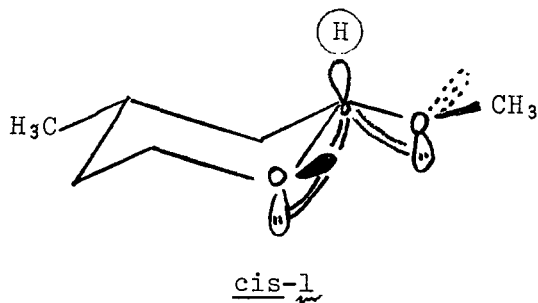
The most interesting aspect of the observed chemistry is that it was found that the cis-isomer of 1 was consumed much more rapidly than the trans-isomer. This was obvious when either the individual isomers or isomeric

mixtures were irradiated. Relative quantum yields are not a good measure of relative rates of excited state processes. In the present system, the lifetime of benzophenone triplet might be different in the presence of the two individual isomers. Therefore, irradiations of mixtures of the isomers in the presence of benzophenone were carried out and the ratio of rate constants for the disappearance of the individual isomers was calculated by the following formula:⁹

$$\frac{k_{\text{cis}}}{k_{\text{trans}}} = \frac{\ln([\text{cis}]/[\text{cis}]_0)}{\ln([\text{trans}]/[\text{trans}]_0)}$$

The ratio was found¹⁰ to be 8.0 ± 1.4 for several samples irradiated for consumptions of the cis-isomer ranging from 70 to 90%. The apparently large variations in the ratio were due to the fact that the function is very sensitive to small changes in the value for the amount of trans-1 remaining.

The greater reactivity of cis-1, which undergoes abstraction of an axial hydrogen atom, can be rationalized nicely in terms of overlap of nonbonding orbitals of both oxygens with the C-H bond being broken. Thus, the cis-isomer has a nonbonding orbital on each of the two oxygens which is antiperiplanar to the bond being broken. The trans-isomer, on the other hand, has only one such



nonbonding orbital antiperiplanar to the bond being broken and, therefore, the transition state leading to the common free radical $\dot{4}$ is stabilized to a lesser degree by orbital overlap. A similar rationale has been offered for ozone insertion in glycosides, where it was found that α -glycosides are inert to ozone while β -glycosides reacted by C-H bond cleavage¹¹ and for specificity of heterolytic C-O bond cleavage in the base catalyzed hydrolysis of esters.¹²

A further contribution to the enhanced reactivity of the cis-isomer may be made by the fact that the cis-isomer is less stable than the trans-isomer. This energy difference has been found to be 0.34-0.73 kcal/mole depending on the solvent.^{3,13} However, since the transition states leading to the common radical $\dot{4}$ are different for the two isomers, it is difficult to evaluate this effect.

Irradiation of the individual isomers of $\dot{1}$ also showed that the initial hydrogen abstraction is irreversible and that the intermediate radical $\dot{4}$ rearranges or loses methyl radical instead of picking up a hydrogen atom from the system, since none of the alternative isomer was found during the irradiations. The reaction step leading to the loss of methyl is presumably irreversible and we are presently looking into the reversibility of the ring opening step in a different model system.

This work adds another chapter to the unfolding story of the many ways in which the oxygens attached to the "anomeric" carbon in carbohydrates and model systems can influence the chemistry of such systems. These effects have been collectively called "the anomeric effect" even though several theoretical interpretations for the various effects have been offered.¹⁴

References and Notes

- (1) Part II of a series "Photochemistry of Carbohydrate Model Compounds." For Part I, see Ref. 2.
- (2) R. D. McKelvey, Carbohydr. Res., 42, 187 (1975).
- (3) C. B. Anderson and D. T. Sepp, Chem. & Ind., 2054 (1964).
- (4) E. L. Eliel and C. A. Giza, J. Org. Chem., 33, 3754 (1968).
- (5) The trans-isomer eluted first on a 1/4" x 5' column of 5% SE-30 on 60-70 mesh Anakrom ABS.
- (6) Benzene solutions which were 0.039M in trans-1, 0.034M in cis-1, and 0.79M in benzophenone were degassed, sealed under vacuum in pyrex, and irradiated for 2-15 hr in a Rayonet Photochemical Reactor with 16 RPR 3000 lamps.
- (7) Products were identified by comparison of gas chromatographic retention times on three different columns and infrared spectra of samples collected off the gc column with those of authentic material prepared by literature methods: S. S. G. Sircar, J. Chem. Soc., 898 (1928); K. C. Mathur and G. S. Saharia, Vikram, J. Vikram Univ., 6 (1), 45 (1962) [Chem. Abstr. 61, 4252c (1964)].
- (8) Although methyl 3-methylvalerate could not be completely separated from trans-1 and small amounts could have gone undetected in the irradiation of the isomeric mixture, irradiation of pure cis-1 in benzene did not give this product. However, this ester was formed in irradiations carried out in t-butyl alcohol, where the formation of 3 is impossible.
- (9) C. Walling and M. J. Gibian, J. Am. Chem. Soc., 87, 3361 (1965).
- (10) Samples were analyzed by gas chromatography on 10% Carbowax 20M on Chromosorb W or 3% OV-17 on Chromosorb Q using acetophenone added after irradiation as internal standard.
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- (14) For leading references, see R. U. Lemieux, K. B. Hendriks, R. V. Stick, and K. James, ibid., 97, 4056 (1975).

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